SF 298 MASTER COPY · KEEP THIS COPY FOR REPRODUCTION PURPOSES

REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	6/18/96	Final 1 Jan 93 - 30 Jun 96

4. TITLE AND SUBTITLE
Synthesis and Polymerization of New Imine Monomers: Azaethylenes, Azabutadienes, and Azaallenes

5. FUNDING NUMBERS
DAAH04-93-G-0013

6. AUTHOR(S)
H.K. Hall, Jr.

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)
Department of Chemistry
The University of Arizona
Tucson, AZ 85721

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
ARO 30588.11-CH

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The synthesis and polymerization of a wide variety of azaethylenes (imines) and azabutadiene were studied. The overall results were modest. Despite systematic manipulation of substituents to favor polymerization, high polymers were obtained infrequently and their physical properties were not outstanding.

Exploratory work led to novel polyaromatic quinonimines. This led to an AASERT project where this work will be described in detail.

14. SUBJECT TERM
synthesis, polymer, imines

15. NUMBER IF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

SYNTHESIS AND POLYMERIZATION OF NEW IMINE MONOMERS:

AZAETHYLENES, AZABUTADIENES, AND AZAALLENES

FINAL PROGRESS REPORT

H.K. HALL, JR.

JUNE 18, 1996

U.S. ARMY RESEARCH OFFICE

DAAH04-93-G-0013

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ARIZONA
TUCSON, AZ 85721

STATEMENT OF THE PROBLEMS STUDIED

AND

A SUMMARY OF THE MOST IMPORTANT RESULTS

Summary

Synthesis and Polymerization of Imines (Azaethylenes and Azabutadienes)

Statement of the Problem - In polymer chemistry the polymerization of olefins (C=C) and carbonyl monomers (C=O) is well established. In contrast, very little monomer-polymer chemistry is known for imines (C=N). A fundamental study of this problem was undertaken. Our approach was to synthesize new C=N monomers. The requirements were that these be isolable and purifiable, yet reactive in addition polymerizations and copolymerizations. Substituents would be kept to a minimum but stabilizing substituents on nitrogen would facilitate anionic radical or cationic polymerization. Our earlier work on the imines and azadienes was reviewed in Makromolekulare Chemie Symposium. [H.K. Hall, Jr. "Synthesis and Polymerization of Imines and Azadienes: New Polymerizable Monomers" Makromol. Chem., Macromol Symp. 54/55, 73 (1992)]" The general indications at that stage was that simple imines were a very limited class of monomers but that the 1-azadienes was a satisfactory new class. More recently we were able to detect C,N-dicyanomethane imine as an exceptionally reactive and fugitive monomer whose presence could be established only by trapping. A family of C-arylimines with several electron-accepting substituents on nitrogen was synthesized. Their attempted polymerizations led only to oligomers. Formaldehyde oxime and its o-benzyl derivatives were examined, but again only low molecular weights were obtained in this case by cationic polymerization. Here cyclic trimer was the product found most often.

As to the azadienes, 3-methyl-N-phenylsulfonyl 1-aza-1,3-butadiene oligomerized anionically and participated in free radical copolymerizations with styrene comonomers. Studies aimed at synthesizing and polymerizing N-cyano-1-azabutadienes proved to be difficult and no real polymers could be obtained.

Summing up all of the above work, it appears that our goal of identifying useful readily available and polymerizable imine monomers has not been met. In general, the monomers are difficult to purify, hydrolytically unstable and do not polymerize high molecular weight materials.

Publications

1993-1995

1. B. Roekens, A.B. Padias, H.K. Hall, Jr., "C,N-Dicyanomethanimine," *J. Chem. Res.* (S) 162 (1993).
2. P.A. Williams, K.A. Ellzey, A.B. Padias and H.K. Hall, Jr. "New Polyaromatic Quinoneimines from Anthraquinone" *Macromolecules* 26, 5820 (1993).
3. P.A. Williams, J.M. Gosau, H.W. Boone, D.K. Park, A.B. Padias and H.K. Hall, Jr., "Novel Polyaromatic Quinone Imines" *Macromolecules* 28, 1 (1995).
4. H.K. Hall, Jr., I. Yahagi, X. Drujon, P.A. Williams, M. Bruck and A.B. Padias, "Syntheses and Structures of Heterocyclic Quinone Arylimines as Model Compounds for Polyaromatic Quinone Imines" *Macromolecules* 28, 9 (1995).
5. H.K. Hall, Jr. "Novel Polyaromatic Quinonimines" *ACS PMSE Preprints* 72, 129 (1995).
6. H.K. Hall, Jr. "Synthesis and Polymerization of Imines and Azadienes: New Polymerizable Monomers" *Makromol. Chem., Macromol Symp.* 54/55, 73 (1992).
7. B.A. Bonner, A.B. Padias and H.K. Hall, Jr., "The Polymerization of 3-Methyl-N-(phenylsulfonyl)-1-aza-1,3-butadiene" *Polym. Bull.* 28, 517 (1992).
8. D.D. Parker, A.B. Padias, and H.K. Hall, Jr. "Synthesis and Polymerization of Azaethylenecarbonitrile Monomers" MS in preparation.
9. D.D. Parker, A.B. Padias, and H.K. Hall, Jr., "Synthesis and Polymerization Studies of Formaldehyde Oximes and its Derivatives" MS in preparation.
10. I.S. Kee, A.B. Padias, and H.K. Hall, Jr., "N-Cyano-1-aza-1,3-butadienes" J. Chem. Res. MS in preparation.